

AN INVESTIGATION OF FUSION MELTED
TITANIUM RICH ALLOYS CONTAINING COPPER

A THESIS

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by
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SUMMARY

Much interest has recently been displayed in the development of titanium as a structural metal. It possesses a number of desirable attributes which render it potentially useful in applications when lightness, strength and good corrosion resistance are required.

This investigation was undertaken to secure information regarding the phase equilibrium diagram of the titanium-copper system. A number of predictions were made regarding the probable nature of the phase equilibrium diagram. On heating, titanium undergoes an allotropic transformation at 1615°F from the low temperature close-packed hexagonal modification to the body centered cubic (beta) form. This transformation will be caused to occur over a temperature range by the addition of another component and the upper temperature limit of the transformation range may be raised or lowered by increasing percentages of that component.

The atomic size factor for the titanium-copper system lies barely within the favorable zone, indicating that any solid solubility of copper in alpha titanium must be of the substitutional variety and will probably be of a low magnitude. Other factors such as the higher valence of titanium and the tendency to form at least one intermediate phase (Cu_3Ti) would also contribute opposing tendencies to the formation of extensive solid solutions.

A consideration of the methods of fabricating titanium base alloys indicated that the special electric arc melting technique would be the

most suitable for this investigation. A furnace was constructed which embodied a water-cooled tungsten tipped steel electrode, a water-cooled copper crucible and provisions for maintaining an inert atmosphere of helium in the melting chamber. Power was supplied by a small D.C. welding generator connected across the steel electrode and the copper crucible. All alloys studied were successfully prepared in this furnace.

Microscopic examination of the alloys in the as-melted condition revealed little information of interest other than the fact that with few exceptions all were reasonably homogeneous. In the annealed condition alloys ranging from 3.94 to 6.27 weight percent copper showed increasing amounts of a dark-etching constituent which was identified as a eutectoid structure by examination at high magnifications. An alloy analyzing 9.83 percent copper was found to lie very near the eutectoid composition. Two-phase alloys in which no eutectoid was visible were encountered in the range 0.97 - 1.81 percent copper. The precipitated phase persisted even after prolonged annealing at 1800°F followed by slow cooling and quenching from temperatures just below the transformation range. Microhardness tests on this phase and the coexisting alpha solid solution showed the precipitated phase to have a much higher hardness (Vickers 430) than the alpha phase (Vickers 307).

Quenching tests were carried out on a number of the alloys and the results obtained were utilized to construct a tentative titanium-copper phase equilibrium diagram for the region 0 - 9.83 percent copper. Typical microstructures are shown and discussed.

It was concluded that the high temperature (beta) solid solution of copper in titanium decomposes eutectoidally upon slowly cooling from

the beta region. The eutectoid temperature was estimated to be 1520°F. Examination of the low-copper alloys in which solid phase precipitation had occurred indicated that the solubility of copper in alpha titanium increases with increasing temperature from a value lying between 0.35 and 0.97 percent copper to a maximum at the eutectoid temperature of slightly less than 1.8 percent copper.

Further work is recommended to evaluate the corrosion and oxidation characteristics of these alloys. Additional studies of the age-hardening and mechanical properties of titanium-base copper alloys might furnish other desirable information.

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I

INTRODUCTION

The Discovery and Occurrence of Titanium

The discovery of titanium is one of the many accomplishments credited to William Gregor (1762-1817), a British clergyman, whose remarkable career also encompassed the fields of mathematics, geology, and mineralogy (4, 57). Gregor reported his find in 1791 and proposed the name menacanite for the new element (57).

Gregor's discovery aroused little interest until 1795 when Klaproth extracted the oxide from a mineral known as "red schorl" (rutile) from Hungary (57). Klaproth acknowledged Gregor's earlier work and affixed the "temporary" name titanium to the new element with the following comment:

"Wherefore no name can be found for a new fossil (element) which indicates its peculiar and characteristic properties, in which position I find myself at present, I think it best to choose such a denomination as means nothing of itself and thus can give no rise to any erroneous ideas. In consequence of this, as I did in the case of uranium, I shall borrow the name for this metallic substance from mythology, and in particularly from the Titans, the first sons of the earth. I therefore call this metallic genus titanium."

Titanium ranks ninth in order of abundance of the elements comprising the lithosphere and accounts for 0.62 percent of the total. It is exceeded in abundance only by oxygen, silicon, aluminum, iron, magne-

sium, calcium, sodium and potassium. Excepting these, it makes up a larger fraction of the known terrestrial matter than all other metals combined, including zinc, copper and lead which are considered quite common (4).

Titanium is a characteristic constituent of igneous and metamorphic rocks. Of 800 igneous rocks analyzed in laboratories of the U. S. Geological Survey, 784 contained the element (4, 57). Titanium dioxide is distributed in soils throughout the world (23) and is present in varying amounts in most clays. The titanates are also widely distributed (4).

Despite its widespread occurrence only a few titanium-bearing minerals occur in bodies large enough to be of economic importance at the present time. Massive ilmenite (mainly ferrous titanate) is found in minable deposits in western Virginia. This deposit occurs in a peculiar rock formation known as nelsonite. Ilmenite is also commonly found associated with iron ores. Along with magnetite it is one of the first minerals to solidify from magmas (4). The largest deposits of titaniferous iron ores in the United States are in the Adirondack Mountains of New York state. Other deposits have been found in Canada, Norway, Russia, Manchuria, Korea, India and the Union of South Africa (2, 4).

Certain beach sands are important sources of ilmenite, rutile (TiO_2) and arizonite (Fe_2TiO_5) (4, 57). Due to the high stability of these minerals, they are left behind as the surrounding rock mass is weathered and eroded away. These placer deposits are easy to work and contribute a large part of the world's output of titanium ores. In the

beach sands of Trovancore, India and New South Wales, Australia, this natural concentration process has progressed to a remarkably high degree. The Monazite sands of Florida contain titanium bearing minerals but not in sufficient concentrations to compete economically with the Indian and Australian deposits (4).

The largest known deposits of rutile are found in Nelson County, Virginia, at Kragero, Norway, and at St. Urbain, Quebec, Canada. Lesser deposits are found in Queensland, Australia; in the island of Madagascar and in Florida and Arkansas. When marketed, rutile concentrates average 94 to 98 percent titanium dioxide (4).

Chemistry of Titanium

An appreciation of certain problems involved in the preparation and fabrication of titanium can best be achieved by considering very briefly some of its pertinent chemical and physical properties. A summary of the physical properties of titanium is in the appendix.

It will be noted first that the metal possesses a rather high melting point (3250°F). This is an obvious disadvantage, because, as will be pointed out later, it necessitates the use of special equipment to perform the melting operation. Another interesting fact is that titanium undergoes an allotropic change. The alpha form which is stable below 885°C crystallizes in the hexagonal system. At temperatures above 885°C, the stable form is the beta modification which is body centered cubic (4, 55, 65).

Perhaps the most striking and troublesome chemical property displayed by titanium is the ease with which it reacts with the atmospheric gases. The existence of four well-defined oxides has been established.

The monoxide, TiO , is feebly basic; the sesquioxide (Ti_2O_3) exhibits decidedly basic properties and the well-known dioxide, TiO_2 , is amphoteric. The trioxide, perititanic acid (TiO_3), exhibits acidic properties only (4, 57).

In the titanates mentioned earlier in connection with the occurrence and ores of titanium, the metal appears as the acidic constituent.

Titanium also displays a high affinity for nitrogen. At least two nitrides are known, Ti_3N_4 and TiN . The latter may be formed by burning titanium in an atmosphere of nitrogen. The mononitride is a bronze-colored compound, having a hardness comparable with the ruby (4). Titanium cyanonitride is also a hard copper-colored crystalline solid which because of its metallic luster was frequently mistaken for the metal itself by early investigators.

There is ample evidence to indicate that titanium forms at least one stable carbide (TiC). Microphotographs of titanium melted in graphite crucibles show that the reaction occurs to some extent by direct combination at the temperature of molten titanium (65).

Titanium will also react with hydrogen gas to yield a hydride (4). The pure hydride is said to be an odorless and colorless gas which burns in air with a colorless flame and deposits titanium dioxide. One gram of titanium will absorb over 400 ml. of hydrogen at room temperature (24).

The Preparation of Ductile Titanium

The production of pure elemental titanium involves many difficulties due to its high melting point and reactivity at elevated temperatures. Many early attempts to prepare elemental titanium resulted in the

formation of nitrides, carbides or cyanonitrides which, because of their luster and metallic appearance, were mistaken for the element. For this reason the early literature on the specific properties of titanium is filled with discrepancies which evidently arose from studies of impure samples.

Hunter (42) was probably the first to prepare the pure element. He described it as a metal resembling steel in appearance, having a melting point of 1800 - 1850°C and a specific gravity of 4.50. The sample was brittle at low temperatures but readily forgeable at red heat.

A number of methods of preparing titanium are in use at the present time. The work of many early investigators indicated that titanium tetrachloride could be reduced with an alkali or alkaline earth metal to yield a spongy product which might be amenable to further purification (51, 59). Kroll (45) reduced titanium tetrachloride with magnesium in a molybdenum lined, electrically heated crucible at 1000°C in an atmosphere of argon. The metal was separated from excess magnesium salts by acid leaching. No alloying of magnesium and titanium was observed and the product was of a reasonable degree of purity. Brace (7) quotes a typical analysis of titanium prepared in this manner, the purity being 97.3 percent. Copper, silicon, iron and vanadium are among the chief impurities.

The process now in use at Boulder City, Nevada by the Bureau of Mines is essentially the same as the Kroll process described above (73). A different method of purifying the reaction product is employed, however. The opened reaction chamber and product are heated in a vacuum retort. The unused magnesium and magnesium chloride either melts or evaporates to leave relatively pure titanium behind. Titanium that has undergone this

treatment is referred to as sponge titanium or "commercial grade" titanium to distinguish it from the purer iodide refined titanium.

So far the production of titanium by the thermal decomposition of the iodide seems to be the most practical means of obtaining small amounts of the pure metal. This process was first described by Van Arkel and DeBoer in 1925 as applied to the production of titanium, zirconium, hafnium and thorium (21). Essentially it involves passing the vapor of titanium tetraiodide over a tungsten filament heated to 100 - 300°C. As long as the temperature of the vapor inside the reaction chamber does not exceed 200°C, titanium will be deposited on the filament according to the reaction $\text{TiI}_4 \rightleftharpoons \text{Ti} + 2\text{I}_2$. Should the temperature rise above this value, another reaction ($\text{TiI}_4 + \text{Ti} \rightleftharpoons 2\text{TiI}_2$) becomes a factor. At 350°C deposition ceases entirely.

There are numerous other methods of preparing titanium, but few of them yield a product as pure or as amenable to purification as the Kroll and iodide processes. It has been suggested that the metal be produced commercially by reduction of the finely divided dioxide with natural gas. The Germans developed three methods of production during World War II. Many attempts have been made to prepare pure titanium by electrolysis of a water or fused salt solution of a titanium compound but results obtained thus far by this method are far from encouraging (4).

Present and Potential Uses of Titanium

Present uses of titanium are well known and include ferrotitanium as a scavenger for steel, as a primary preceptation hardening element, and as a ferrite former (74). It has been widely employed as a stabilizing constituent in austenitic stainless steels. By its action with

carbon to form a carbide it prevents intergranular corrosion (67).

The potential uses of titanium are based mainly upon such favorably combined properties as high strength, light weight and excellent corrosion resistance. This suggests its use not only as a substitute for presently used strategic metals, but also for construction materials having a combination of properties not possessed by other available metals and alloys (62).

The purest titanium yet made available for testing and experimentation is that refined by the iodide process described earlier. This material is characterized by low hardness, ability to be drastically cold worked, relatively low yield and tensile strengths and high elongation (31). Commercial grade (magnesium reduced) titanium shows ultimate and yield strengths approximately twice as great as iodide titanium, both in the annealed condition. This variance in mechanical properties may be explained by the presence of higher percentages of impurities in the commercial grade titanium. A comparison of the mechanical properties of these two types of titanium is given in the appendix.

A comparison of the above properties with those of aluminum and iron reveals some interesting information. Titanium has a density (4.5 gm/cc) intermediate between that of iron (7.9 gm/cc) and aluminum (2.8 gm/cc). In the annealed condition, the ultimate strength of titanium compares favorably with that of annealed 18 - 8 stainless steel. Other data indicate that titanium is elastically stable and retains its strength at temperatures in excess of 800°F. This compares very favorably with the best aluminum alloys which ordinarily are not used to any great extent above 400°F.

Laboratory tests on titanium's chemical corrosion resistance indicate that the metal is resistant to nitric acid of all concentrations, warm dilute hydrochloric and sulphuric acids, aqua regia, chlorine and sodium hydroxide. Its sea water and marine atmospheric corrosion resistance are truly outstanding. In this field it should be ranked with platinum and Hastelloy C. (9).

In summary, titanium fills a gap between aluminum alloys and stainless steels, combining certain desirable properties of both. These properties indicate that it might be useful in many situations where light weight, corrosion resistance, high strength and intermediate temperature properties are required.

Titanium Base Alloys

As will be shown later, the atomic size of titanium is such that it could be expected to alloy readily with many of the common metals. In the hope that the already desirable properties of the metal might be enhanced by alloying additions, much work has already been undertaken in that direction. Larsen et al (50) investigated titanium alloys of hydrogen, beryllium, boron, aluminum, indium, carbon, silicon, zirconium, nitrogen, vanadium, oxygen, chromium, molybdenum, tungsten, manganese, iron, cobalt, and nickel. Aluminum and beryllium alloys of titanium were found to hot and cold roll readily and the aluminum-titanium alloys displayed a greatly increased resistance to oxidation over that of pure titanium. Manganese in relatively small percentages greatly increases the tensile strength of titanium. Silicon alloys (0.5 - 1 percent Si) in the cold rolled condition exhibited noteworthy mechanical properties.

Other binary alloys were studied by Craighead, Simmons and East-

wood who concluded that the best properties of most titanium alloys are displayed in the as hot-rolled condition (15). Some of the systems they investigated were found to respond to solution heat treatment.

The same investigators made a study of 113 ternary and 84 quaternary alloys of titanium (16, 17). They found that the addition of 0.25 percent carbon in the ternary alloys investigated produced some improvement in the tensile strength of the alloys in the hot-rolled condition without a serious decrease in ductility. Many of the quaternary alloys containing chromium were found to harden appreciably after hot rolling and aging.

These investigations have all been of an exploratory nature. Much more experimentation lies ahead before alloys can be developed for specific applications. The overall picture, however, is encouraging at this stage.

It is hoped that the experimental work described in this thesis will shed some light on the nature and properties of titanium-copper alloys.

II

THEORETICAL CONSIDERATIONS

Solid Solutions

The early work on equilibrium diagrams made it clear that in many alloy systems the addition of one metal to another did not always produce a second phase but resulted in the formation of a homogeneous alloy which was regarded as a solid solution of one metal in the other.

Metallic solid solutions may be conveniently grouped into two classes - interstitial and substitutional. In the first of these (the more infrequent type), the solute atoms are found to occupy the voids or interstices between the atoms of the solvent metal. It is evident from the configuration of such a solution that only solute atoms of relatively small diameter are capable of dissolving interstitially. The principal elements which display this behavior are carbon, hydrogen, nitrogen and boron (22, 39, 69).

In the substitutional type, the atoms of the solvent metal are replaced in the space lattice of the solvent metal by the atoms of the solute metal. It is with this type of solid solution that we are concerned in a study of titanium-rich alloys of the titanium-copper system (62).

In crystals of a pure metal, each point in the space lattice is occupied by the same kind of atom. To picture the formation of a substitutional solid solution, we may visualize these solvent metal atoms as being crowded out of their space lattice by the solute atoms. The solute atoms then assume the positions vacated by the solvent atoms.

This substitution is usually random, but there are cases where the solute atoms assume definite positions in the solvent metal space lattice upon slowly cooling or annealing at a low temperature. This modification of the substitutional solid solution is given the name superlattice (39). Superlattice formation is encountered in relatively few alloy systems.

The formation of a substitutional solid solution is generally accompanied by an expansion or contraction of the lattice parameter of the solvent metal (22, 39). This is shown by the fact that the lines or spots on X-ray diffraction photographs of solid solutions are displaced from the positions they occupy in the diffraction pattern of the pure metal solvent. The overall pattern, however, remains the same since both the solid solution and the solvent metal have the same crystal structure. To a first approximation, this deformation of the solvent metal space lattice is proportional to the atomic percentage of solute metal. This proportionality is known as Vegard's Law (71). It implies that for two completely miscible metals, the lattice parameter-composition curve would be a straight line joining the lattice parameters of the pure metals. What usually occurs, however, is a smaller variation of the lattice parameter with composition than would be predicted from Vegard's Law (39).

Hume-Rothery (38, 39, 40, 41) has discussed in great detail the factors influencing the formation and extensiveness of substitutional solid solutions. He and his co-workers have concluded that if the difference between the atomic diameters of the solute and solvent metals expressed as a percentage of the atomic diameter of the solvent metal is greater than 15, solid solubility will in general be very restricted.

For percentages lower than the above value extensive substitutional solid solutions may be formed subject to limitations to be described later. The atomic diameters used above refer to the closest approach of the atoms in the pure metal and the percentage thus obtained is termed the atomic size factor. Complete miscibility in the solid state is possible only if the two metals involved possess the same crystal structure and a favorable atomic size factor.

Intermediate Phases

A factor operating against the tendency of two metals to form extensive primary solid solutions is the ease with which they form stable intermediate phases at the expense of such solutions (22, 38, 39, 69).

The term "intermediate phase" in its broadest sense refers to all new phases between the solubility limits of the primary or terminal solid solutions. These intermediate constituents sometimes conform to definite atomic ratios and may be conveniently designated by chemical formulae, e.g., Cu Al , Cu_5Zn_8 and Mg_2Sn . Such intermediate phases that show only limited variation in composition are called intermetallic compounds (22). The more electronegative the solute element and the more electropositive the solvent (or vice versa), the greater will be the tendency to form stable intermediate phases. A thermodynamic consideration of such phases shows that they invariably possess a much lower thermodynamic potential than solid solutions and will therefore form in preference to solid solutions when a choice exists between the two (69). One of many examples that might be cited is the system magnesium - antimony. Despite the fact that the atomic size factor is favorable, the solubility of antimony in magnesium (and vice versa) is very slight due to the formation of the

stable compound Mg_3Sb_2 (39).

These intermediate phases often exhibit properties radically different from those of the component elements and frequently assume quite complex crystal structures. For instance, the gamma brass (Cu_5Zn_8) phase has a complex cubic structure which requires 52 atoms to describe its symmetry (22). The lower order of crystal symmetry and fewer planes of dense atomic population appear to be associated with these differences in properties, e.g., greater hardness and lower thermal and electrical conductivity.

The following empirical rules regarding intermediate phases may be cited (39):

(1) There is a general tendency for all metals to form normal valence compounds with the elements of groups IVB, VB and VIB of the periodic classification. A normal valence compound is simply one in which the metal exerts its normal valence, i.e., the valence one would expect it to possess by virtue of its electronic structure.

(2) This tendency and also the stability of the compound is greater the more electropositive the metal and the more electronegative the element from group IVB, VB or VIB.

The Hume-Rothery Rule

Numerous other intermediate phases have been studied wherein the metals involved do not appear to exercise their normal valence. When compounds are formed from two metals, it hardly seems possible that the components, both of which are electropositive, would exhibit their normal valencies. A classification of intermediate phases (other than normal valence compounds) by assigning to each component element a definite

valence is therefore impossible.

Another classification however has been studied by Hume-Rothery and co-workers (38, 39). First it will be noted that in alloys of copper and certain other monovalent metals with elements of the B sub-groups the general configuration of the thermal equilibrium diagram is the same. Copper alloys of aluminum, zinc and tin have been studied extensively. It was found that in all three alloy systems the primary copper-rich solid solution (α) gives way, with increasing solute content, to a two phase ($\alpha + \beta$) region which is followed by another homogeneous (β) region. Many alloy systems follow this pattern and there actually appears to be a periodicity in the alloys of copper, silver and gold with the B sub-group elements. Choosing, for example, the familiar copper-zinc system, we find that the primary (α) phase is a solid solution of zinc in copper and therefore possesses the face-centered cubic structure of copper. The β phase is a body-centered (Cs Cl) type of cubic crystal and the ϵ phase is nearly hexagonal close-packed. The other primary phase, η , is a solid solution of copper in close-packed hexagonal zinc. The same phase sequence may be observed in other alloys of copper, silver and gold with elements of the B sub-groups (69).

One thing in common which certain intermediate phases in the above systems possess is their occurrence at definite ratios of valence electrons to atoms. For example when copper is alloyed with zinc, the β phase occurs in the region 50 atomic percent of zinc (CuZn). In the Cu-Al system, the β phase falls at roughly 25 atomic percent aluminum (Cu_2Al), and with tetravalent tin the β phase lies at 16 atomic percent of tin (Cu_5Sn). In CuZn , there are three valence electrons - one from the

copper atom and two from the zinc. There are two atoms, so the ratio of valence electrons to atoms is 3:2. By making the same calculations for the Cu-Al and Cu-Sn systems, we find that for this series of alloys the beta phase appears at such concentrations that the above ratio of valence electrons to atoms is maintained. Similarly, the gamma phases of these systems have been found to occur at an electron: atom ratio of 21:13. The gamma phases assume a complex cubic arrangement typified by gamma brass (see page 13), while the 3:2 beta phases generally occur in the body-centered cubic crystal habit. Finally, the epsilon phases which occur with an electron: atom ratio of 7:4 all possess a hexagonal crystal lattice (39, 69).

The above findings, now known quite universally as the Hume-Rothery Rule, were originally deduced for alloys of the monovalent metals with the B sub-group elements. Electron compounds do not appear to be restricted to these systems, however. Beta compounds displaying both the 3:2 electron: atom ratio and the body-centered cubic structure have been observed in the silver-magnesium and gold-magnesium systems. Transition elements are also capable of forming electron compounds, for example FeAl, NiAl, $\text{Ni}_5\text{Zn}_{21}$ and FeZn_7 (5). These observations do not indicate that there is any rigorous means of establishing prior to experimentation whether or not two given elements will form such a compound.

The formation of any or all of the possible electron compounds or other intermediate phases between components of a system contributes an opposing tendency to the formation of extensive substitutional solid solutions. This electronegative valency effect is operative along with the atomic size factor and the crystallographic nature of the substances

involved and has been given due consideration for the Ti-Cu system.

The Relative Valency Effect

Still another factor affecting the configuration of thermal equilibrium diagrams is the relative valency of the components. A survey of the more reliable data has led to the conclusion that, other things being equal, a metal of lower valency is likely to dissolve more of a higher valence metal than vice versa (39, 69). An example often quoted is the system Cu-Si, wherein silicon crystallizes in such a way that each silicon atom has four close neighbors. The structure of silicon is built up by each atom sharing one of its electrons with each of the four neighboring atoms thereby forming stable homopolar bonds. If, in this structure, an atom of silicon is replaced by one of copper, there will be insufficient electrons to form covalent bonds, and consequently solid solubility will be restricted. There are exceptions to this rule, but it is generally true for alloys of the univalent metals with those of higher valency.

Allotropic Transformations

Inspection of alloy systems involving polymorphic metals indicates that the transformation temperature of a metal undergoing such a phase change may be either raised or lowered by the addition of a solute metal (22). This is of importance in the system under consideration since titanium undergoes an allotropic transformation.

Evaluation of the Ti-Cu System

Application of the foregoing principles to the titanium-copper system poses many problems which will become apparent later.

With reference to the solubility of copper in titanium, indications

are that it should be of a rather low magnitude. Alpha titanium exists in the close-packed hexagonal crystal lattice (12, 22, 55) while copper belongs to the face-centered cubic system (22). This crystallographic dissimilarity precludes any possibility that the two metals may be completely miscible in the solid state. The atomic diameters of titanium and copper are given as 2.90 and 2.55 angstroms respectively (22). The atomic size factor for the system is thus $100 (2.55 - 2.90) / 2.90 = -12$. This is barely within the somewhat arbitrary favorable zone fixed by Hume-Rothery et.al. and consequently this system must be considered a borderline case. However, it is obvious that any solid solubility which does occur will be of the substitutional variety.

Another complicating factor is the doubt which appears to exist as to the electronic configuration assumed by titanium in its alloys. Hume-Rothery states that titanium is capable of existing in the 2-8-8-4 configuration in some of its alloys rather than in the 2-8-10-2 structure (39).

It has been pointed out that the formation of stable intermediate phases tends to restrict solid solubility. On the basis of the two empirical rules governing the formation of normal valence compounds we may discount the possibility of this type of intermediate phase existing in the titanium-copper system. Electron compounds such as those observed in alloys of copper, silver and gold with the B sub-group elements might very well exist in the case of titanium, although titanium is not a B sub-group element. An exhaustive survey of the literature revealed that at least one such compound exists in the titanium-copper system, namely the epsilon compound which has the formula Cu_3Ti and crystallizes in the

typical epsilon hexagonal space lattice (72). The epsilon electron: atom ratio (7:4) is obtained for the above compound if titanium is assumed to be present in the tetravalent 2-8-8-4 form. It is a simple manner to calculate the formulae of the other two possible electron compounds. For the gamma (21:13) compound the following relations must obviously hold true.

$$\begin{aligned} X + Y &= 13 \\ 4X + Y &= 21 \end{aligned}$$

X and Y are the number of titanium and copper atoms respectively associated with one hypothetical molecule of the compound. Solving the equations gives $X = 8/3$ and $Y = 31/3$. The simplest formula for the gamma phase is therefore $\text{Cu}_{31}\text{Ti}_8$. In a like manner the formula Cu_5Ti may be derived for the beta (3:2) compound. It is interesting to note that an identical series of three electron compounds is formed in the system Cu-Sn(10). In the Ti-Cu system, however, the epsilon (Cu_3Ti) compound is the only one which is definitely known to exist.

Application of the relative valency rule is complicated by the same question as the electronegative valency effect, namely the doubt as to which electronic configuration titanium assumes in its copper alloys. The electron compound described above lends substance to the belief that titanium acts as a tetravalent element. The relative valency rule would therefore restrict the solubility of copper in titanium to a smaller magnitude than the solubility of titanium in copper.

Very little can be said of the effect of copper content on the transformation temperature of titanium-rich alloys. There are a number

of possibilities, some of which have been observed in alloys of titanium. The solute may form an extended solid solution with the high temperature beta allotrope of titanium. The solubility in alpha titanium may then increase with decreasing temperature from zero at the transformation temperature to some maximum value at room temperature while the transformation temperature decreases with increasing solute content. Or the high temperature titanium-rich solid solution may decompose eutectoidally upon cooling. An example of this type of behavior would be the decomposition of austenite into ferrite and cementite in the familiar iron-carbon system. A preliminary examination of the titanium-nickel system indicates that the high temperature titanium-rich solid solution decomposes in a eutectoid reaction which occurs at approximately 760°C (52).

Both of the above possibilities have been described by Gonser, who shows the type of equilibrium diagram obtained in each case (30). Still another possibility exists - the formation of a peritectoid such as may be found in the titanium-nitrogen and titanium-carbon systems (58). This situation however is quite rare.

In summary, the factors which have been considered indicate that the solubility of copper in titanium will be slight and should be less than 5 atomic percent which is the maximum solubility of titanium in copper (35). This restricted solubility is brought about by the borderline atomic size factor for the system, the higher valence of titanium and the tendency to form at least one intermediate phase. If certain reliable data were available regarding alloys of titanium, it would be possible to make an actual numerical prediction as to the form of the solvus curve by utilizing the electron concentration rule of Hume-Rothery

(39, 41). However, the lack of such data does not warrant the extension of the theory of alloys beyond this point.

III

PRACTICAL CONSIDERATIONS

Problems Involved in the Fabrication of Titanium Alloys

It has been pointed out that titanium is a member of a periodic group of the elements which is characterized by high affinity for certain of the common gases. This constitutes a serious difficulty in fabricating titanium and its alloys and therefore merits consideration here.

At a temperature of 800°C, titanium will ignite spontaneously in an atmosphere of pure nitrogen. This is the only known actual combustion that occurs in nitrogen (49). Ignition occurs at a lower temperature in oxygen. It is evident that both of the above gases must be excluded from the melting chamber.

Melting titanium in atmospheres contaminated with relatively small amounts of the atmospheric gases usually results in the formation of sufficient quantities of the oxides and nitrides to seriously embrittle the resulting ingot (10, 36, 43). This contamination is dramatically evidenced by the change in mechanical properties of iodide titanium upon alloying it with oxygen or nitrogen (43).

The hardness of iodide titanium is increased from 120 (Vickers) to 240 - 260 (Vickers) upon the addition of one atomic percent of oxygen (2.5 wt. percent) or nitrogen (2.2 wt. percent). The tensile strength is also increased, with nitrogen perhaps exerting the greatest influence. Complete exclusion of oxygen and nitrogen during the melting of titanium and titanium base alloys is therefore necessary if it is desired to produce alloys which possess mechanical properties truly representative of

the system under investigation.

Indications are that titanium and titanium base alloys can be annealed at moderately high temperatures in air without serious contamination. Some superficial scaling occurs at temperatures near 1000°F but it appears that the rate of diffusion of oxygen inward from the surface of massive specimens is immeasurably low under these conditions. At temperatures between 1400 - 1600°F the oxide-nitride film eventually attains a thickness of roughly four thousandths of an inch (8). It is maintained by some investigators that this film formation inhibits further diffusion, although oxide films formed in excess of 1800°F exhibit a tendency to spall (10). Actual combustion in air occurs at a temperature of about 2200°F (4).

Titanium also exhibits a strong affinity for hydrogen (24, 28, 34). Kroll (45) reports that hydrogen is soluble in titanium to an atomic ratio of hydrogen to titanium of 1.73. The absorption of hydrogen by titanium is completely reversible. The absorbed gas may be removed by heating in vacuo to 1850°F (50). The evolution of absorbed hydrogen occurs with considerable violence when the titanium is heated rapidly to a high temperature as in the electric arc melting process to be described later, and severe contamination can occur by the splashing of molten titanium upon the electrode as the hydrogen is evolved. Fortunately large concentrations of hydrogen are encountered only in certain grades of acid-leached titanium (65). Magnesium-reduced titanium which has been further purified by vacuum distillation does not contain absorbed gases in amounts detrimental to rapid fusion. Two obvious methods suggest themselves for excluding the atmospheric gases during the melting of titan-

ium and both have been widely employed. Titanium and other refractory metals have been melted in high vacuum induction and resistance furnaces with varying degrees of success (47, 68). Static and moving inert atmospheres have also been employed with argon generally finding preference as the inert gas (36, 65).

With the elimination of the atmospheric gases as sources of contamination, there still exists the problem of finding a suitable refractory crucible material. Attempts to melt titanium in the usual refractories have ended disastrously. Early experimentation clearly indicated that silicate-bonded materials were completely out of the question (65). Both the heat of oxidation and the melting temperature of titanium are relatively high and in the molten state titanium reacts with most of the common refractory oxides. Kroll has reported that MgO , CaO and Y_2O_3 react readily with molten titanium (45). A recent comparison has been made of the oxides of aluminum, beryllium and thorium to determine the extent of their utility (7). It was found that titanium reacts exothermically with alumina and to a lesser extent with beryllium oxide to yield a hard brittle substance radically different from titanium. With thorium oxide the reaction occurred to only a slight extent and some success has been achieved by melting titanium in specially processed thoria crucibles (8). Graphite crucibles have been used but a variable carbon "pick-up" (0.5 to 1.5 percent) inevitably occurs (50).

In summary, the main difficulties encountered in the fabrication of titanium alloys are the possibility of contamination by the atmospheric gases and the reactivity of molten titanium with most of the common refractory oxides. The atmospheric gases may be excluded by an inert at-

mosphere or a high vacuum but a suitable refractory crucible material has not yet been developed. As will be shown later, the use of any refractory material can be avoided by substituting a water cooled metallic crucible.

Fabrication of Titanium Alloys

Titanium-base alloys have been fabricated by a number of methods while simultaneously eliminating or minimizing contamination from sources mentioned earlier. The standard powder-metallurgy techniques have been used for the production of experimental specimens (50). Titanium powder is intimately mixed with any powdered alloying additions and put in a hardened steel die. The powder mixture is then subjected to a high pressure at room temperature or above. Pure titanium has been consolidated satisfactorily by compressing the powder to 50 tons per square inch at 1000°C for 16 hours in a high vacuum (2×10^{-4} m.m. Hg). Another group of investigators employed a pressure of 30 tons per square inch at room temperature and sintered the compacted mass for one hour at 1200°C in a vacuum of less than one micron (50).

Certain disadvantages are inherent in the powder metallurgy method. The high pressures required necessitate the use of special equipment which was not available for this investigation. Alloys produced in this fashion invariably exhibit a certain amount of porosity. Micro structures of titanium-copper alloys in the as-sintered condition show a large amount of porosity which can be removed only by cold working and annealing (52).

The Bureau of Mines has developed a novel variation of the powder metallurgy method which circumvents the restrictions imposed by high compacting pressure and vacuum sintering (52).

Essentially the method consists of sealing the powdered titanium in welded metal sheaths and working the assembly at elevated temperatures. Metal prepared in this manner is dense and sound in contrast to the porous mass obtained by the usual pressing and sintering operations. Its mechanical properties and microstructure are comparable with those of sintered titanium which has been worked and annealed.

The metal containers for sheath rolling may be made of any suitable material, iron being the one most generally used. The sheaths perform two primary functions, namely, they provide protection from the atmospheric gases and confine the powder particles during the working operation. This confining action serves to distort the individual particles during working, which ruptures any surface films that may be present and insures good contact between the particles so that diffusion and welding into a dense coherent mass may occur. The sheaths are readily removed from the finished piece by cutting the ends and sides and stripping the sheath off. Any contamination from the sheath is quite minor and may be removed by simple pickling.

This method of alloy fabrication, now known widely as sheath rolling, has definite advantages over the normal pressing and sintering operations. Larger and denser specimens can be made in this fashion and the method has been extended to other metals and alloys (52). However certain special equipment is required for the rolling operation and the temperature at which the rolling operation is carried out must be closely controlled.

Still another means of obtaining small amounts of titanium alloys with negligible contamination is now in use. Historically the method was

developed by Von Bolton, who in 1903 arc melted Tantalum buttons on a water-cooled copper plate (3). Many later modifications of the apparatus he used have been developed. Most of them embody the following features (65):

- (1) The employment of an inert atmosphere.
- (2) A water-cooled, inert tungsten-tipped electrode.
- (3) A water-cooled copper crucible.

Arc melting has achieved considerable success commercially in the consolidation of titanium and titanium-base alloys. The use of an inert atmosphere prevents atmospheric contamination and the refractory problem is entirely circumvented. Molten titanium does not wet or adhere to the water-cooled copper crucible. Despite expectations to the contrary, arc melted alloys have proven to be fairly homogeneous except for certain alloys of titanium with the more refractory metals (65).

It appears that this method is the simplest and most readily adopted means of producing small ingots such as will be required in this investigation.

The Metallography of Titanium

The optical metallography of titanium promises to be very complex. It has many microstructural analogies with iron and exhibits certain peculiarities of its own (63).

Two facts have already been mentioned which are pertinent to a study of titanium's metallography. First, titanium undergoes an allotropic transformation at 1625°F from the hexagonal close-packed low temperature phase to the high temperature-body-centered-cubic form (4, 55, 65). The reactivity of titanium at high temperatures has already

been discussed in some detail. It follows that transformation products may be present in the microstructure, as well as varying amounts of other phases, depending upon the purity of the specimen.

Much confusion arises from the fact that titanium deforms at room temperature by both slip and twinning (63). The twinning phenomenon occurs along certain preferentially oriented planes of dense atomic population and sometimes results in the formation of a series of evenly spaced lines or striations across grains of alpha titanium. This is easily confused with Widmanstatten precipitation, and in extreme cases may obscure the true microstructure. Care must be exercised during the polishing operation to minimize slip and twinning.

A number of etching reagents have been employed for titanium and its alloys. Hydrofluoric acid is the most effective etchant reported thus far. The following reagents have been used by the Remington Arms Company (63);

(A-etch) 1 part by volume 48 percent hydrofluoric acid.

1 part by volume concentrated nitric acid.

2 parts by volume glycerol.

(B-etch) 1 part by volume 48 percent hydrofluoric acid.

1 part by volume glycerol.

A-etch has been found to be particularly useful for developing grain boundaries of alpha titanium. The hydrofluoric acid attacks the metal; the nitric acid brightens the surface by removing stain and residue and the glycerol serves as a vehicle and moderator. If it is desired to eliminate the brightening effect of the nitric acid, Betch is employed. This reagent darkens alpha titanium drastically but only outlines beta

titanium.

Other investigators have employed similar reagents differing from the above only by the substitution of water for glycerol (52). When water is used, the concentration of the acids must be reduced.

Previous work on the Titanium-Copper System

As early as 1931, investigators in this country studied copper-rich alloys of this system. Hensel and Larsen (35) prepared a series of alloys ranging in composition from 0.83 to 27.3 weight percent of titanium in a high-frequency induction furnace. The titanium they used was appreciably contaminated with iron, aluminum and silicon and the melting operation was carried out in an air atmosphere. In addition to investigating the age-hardening characteristics of the copper-rich alloys, they proposed a tentative titanium-copper thermal equilibrium diagram based on thermal data. They found the melting point of copper to be lowered by titanium additions down to 1610°F where a eutectic reaction apparently takes place. The eutectic composition was estimated to be between 20 and 27 percent of titanium. The solubility of titanium in copper was found to increase from 0.40 percent to 4 - 4.5 percent titanium at the eutectic temperature. X-ray data indicated the existence of a compound of titanium and copper.

Schumacher and Ellis (64) had previously found copper-rich titanium alloys to be age-hardenable. They used titanium of considerably higher purity than that of Hensel and Larsen but the validity of their data is open to question. Several of their alloys were prepared by fusion in an atmosphere of hydrogen.

Kroll (46) submitted evidence regarding the equilibrium relationships of copper-rich alloys of titanium based upon resistance and hard-

ness measurements. His findings are in substantial agreement with those of Hensel and Larsen.

A survey of the titanium-rich alloys of this system prepared from process A titanium has shown that these alloys also respond to solution heat treatment (15). Additions of copper up to 5 percent lowered the transformation temperature of titanium. This evidence strongly suggests that the high-temperature titanium-rich solid solution decomposes eutectoidally upon cooling, a possibility that was recognized earlier.

IV

EXPERIMENTAL APPARATUSFurnace Design and Equipment

A consideration of the methods of fabricating titanium-base alloys strongly indicates that the most feasible means of producing small specimens of the desired purity is by the use of the special arc-melting technique described earlier. All alloy specimens studied in this investigation were prepared by that method.

There have been in the past almost as many furnace designs as there have been investigators. However all furnaces embody the features listed in Chapter III.

The most significant industrial application of this special arc-melting technique was developed by the M. W. Kellogg Company recently. Generally known as the "electric-ingot" process, it was widely utilized for the production of special alloy steels during World War II (13). Investigators in the Climax Molybdenum Corporation's laboratory have arc-melted molybdenum ingots from 3 to 4 inches in diameter and weighing up to 60 pounds (61). In addition to the usual features, the above commercial processes employ a consumable electrode. Such an electrode is usually fashioned by powder metallurgy from powder of the metal to be melted. The electric arc is struck between this electrode and the crucible bottom and the sintered electrode gradually melts as it is fed into the furnace. The molten metal collects and solidifies in the crucible. A furnace employing a consumable electrode may, as in the Climax Molybdenum Corporation's vacuum arc-melting process, be operated semi-batchwise.

The powdered charge may be forced by a screw-feed arrangement through electrical contacts to accomplish the sintering operation. The sintered electrode is then fed directly into the furnace where melting is in progress. The consumable electrode eliminates the need for water cooling at that point and the slight but persistent contamination that results from the use of a non-consumable electrode. On the other hand, it is not always easy to prepare intimate powder mixtures of the alloy's components. It is obviously necessary to prepare such a mixture for each alloy composition required. Due to the rather large number of specimens required for this investigation a batch-type furnace was used.

The essential elements of the furnace are shown in Figure 1. Two standard pipes machined down to the indicated dimensions served as the furnace walls, and provisions were made to insure a steady flow of cooling water through the annular space during the melting operation. The water cooled electrode was constructed from a 1/4 inch standard steel pipe with a tungsten tip nickel-brazed to the lower end. This type of electrode was found to have a longer life than a number of others made from copper and brass tubing with the tungsten tip silver-soldered to the tubing. The crucible was a 7" diameter 19/32" gauge disc of Anaconda cold-rolled electrolytic copper with a conical depression machined to hold the charge. The electrode was supported above the crucible by a rubber diaphragm gasket with a hole in its center which was slightly smaller in diameter than the electrode. This insured a tight fit around the electrode and minimized gas leakage. This arrangement permitted the electrode tip to be moved at will by the operator while watching the melting operation through the sight glass.

• *Chrysomelidae* (Coleoptera) (Insecta)

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• *Chrysomelidae* (Coleoptera) (Insecta)

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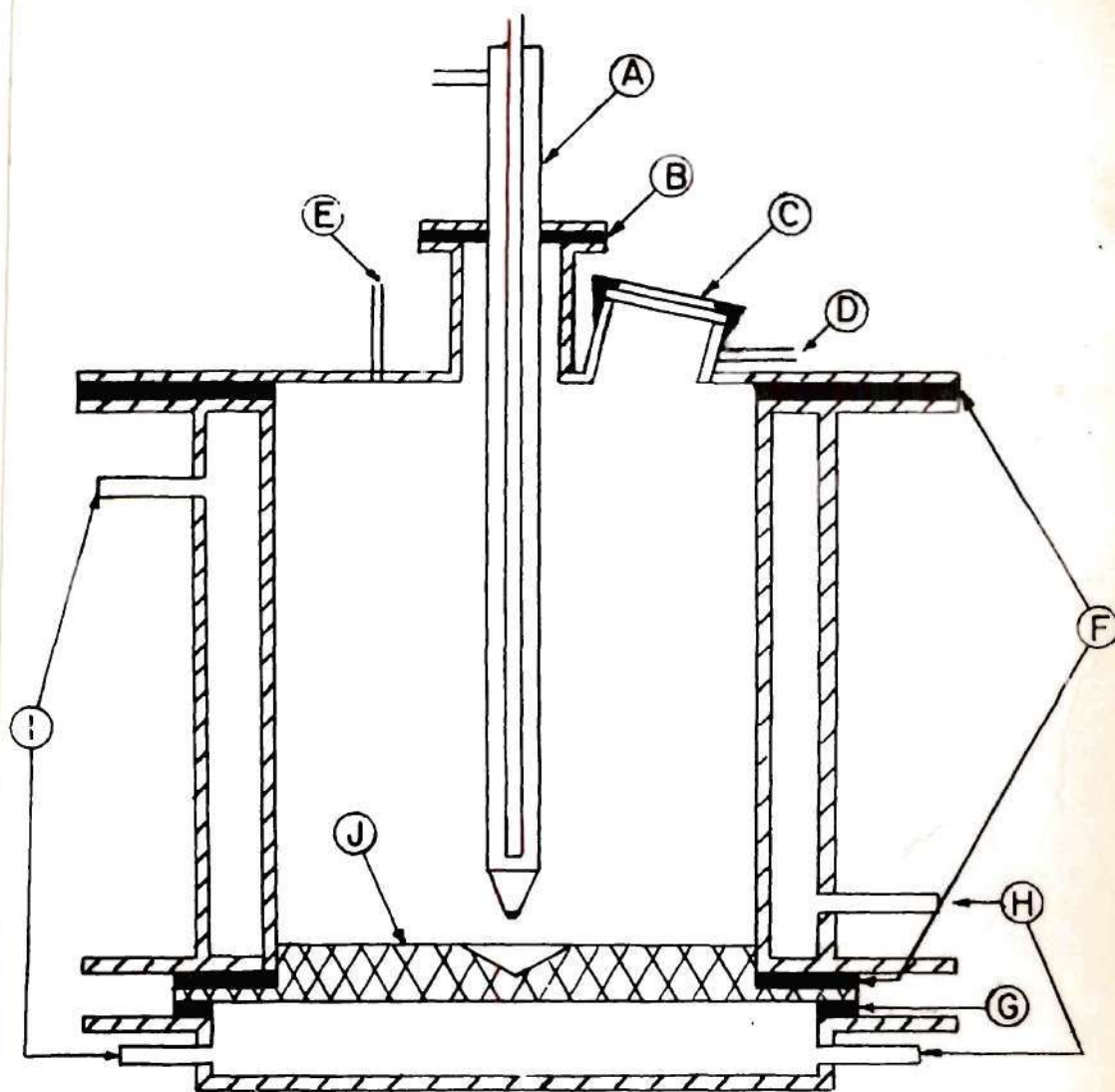


FIGURE 1
SPECIAL INERT ATMOSPHERE
ELECTRIC ARC FURNACE
SCALE : 1"=2"

FIGURE 1

Tank helium was used as a protective atmosphere during melting and functioned satisfactorily. The helium flow rate was adjusted by a standard type of helium regulator and a slight positive pressure of helium was maintained in the furnace by causing the exit helium to flow through a two inch head of water in a glass bubbler.

Three pounds of sponge (commercial grade) titanium was available for use on this project. Alloying additions of copper were made in the form of 10 mil copper wire. Most other investigators have used powdered titanium as a charge for arc furnaces of this type. Small (1" dia.) lumps of sponge titanium, however, proved to be less susceptible to scattering when the arc was struck and were employed throughout this program.

The power source used was a small Wilson "wasp" D.C. welding generator (25V., 150 amps.). Other investigators have employed much higher currents but in so doing have used larger electrodes and melted larger ingots. The above generator was found to be suitable for melting the small specimens required for this work. The electrode was held in a standard welding electrode holder.

Furnace Operation

A typical heat was made as follows: the desired proportions of sponge titanium and copper wire were weighed on a rough laboratory balance and placed in the copper crucible. The furnace top was then bolted on and the electrode gripped in the holder and inserted through the gasket. The helium regulator was then opened and the entire system flushed for at least three minutes. At the end of this period the helium outlet tube was connected to the glass bubbler and a positive pressure of helium in

the furnace equivalent to two inches of water was maintained. The generator was set on high tap, 160 amperes, and the arc was struck. The electrode was manipulated so as to keep the charge in the molten condition for at least one minute.

The furnace described above, as finally derived from a few experimental runs, functioned satisfactorily.

Testing Procedure

After melting, the ingots were given a homogenization anneal and cut into pieces on a cut-off wheel for subsequent microscopic examination. The polishing procedure necessitated first the grinding away of any oxygen and nitrogen-rich surface layer followed by lapping with the following grades of emery paper: 1, 0, 2/0 and 3/0. It was found advantageous to keep the last two emery papers covered with a film of paraffin in mineral oil during the polishing operation. This was followed by lapping on canvas wheels with 400 and 600 grit silicon carbide suspensions and levegated alumina on felt. For photographic work the specimens were given an additional lapping on a slowly-moving felt wheel with a magnesia suspension.

Following this operation the specimens were examined with the Bausch and Lomb research metallograph.

Hardness testing was performed on a Rockwell superficial hardness tester. Later in the investigation it was found desirable to utilize the Bergsman microhardness tester which made possible hardness measurements on individual phases in two phase alloys.

V

EXPERIMENTAL METHODS AND RESULTS

Determination of Phase Boundaries

There are at least two methods of determining phase boundaries in thermal equilibrium diagrams. In the so-called optical method as applied to the determination of solvus lines, several specimens of a given alloy are annealed for homogenization at a temperature a little above that at which the maximum solid solubility occurs and cooled slowly. Individual specimens are taken from the furnace at predetermined temperatures and quenched. Examination of a series of specimens which have been accorded the above treatment for the presence of a precipitated phase makes possible an estimation of a point on the temperature-solid solubility curve. Repetition of this process, using alloys of different compositions enables one to construct the solvus line. By a similar process, other phase boundaries may be located (22, 26, 27).

The X-ray method relies upon a property of most metals discussed in an earlier chapter, namely the expansion of the solvent metal's lattice parameter(s) which accompanies the formation of a substitutional solid solution (1, 11, 22, 26, 27, 35, 69, 70). To locate a solvus line by this method one first obtains a lattice parameter-composition curve. An alloy which lies barely within the two-phase region is then quenched from successively higher temperatures and the lattice parameter of the solvent metal determined at each temperature. The compositions corresponding to these parameters on the lattice parameter-composition curve are the solubilities at the quenching temperatures. This is the parametric method for determining solvus

lines. A similar technique known as the disappearing phase method is used to locate other phase boundaries (1).

The X-ray methods are valuable tools for precision measurements, but the interpretation of X-ray diffraction photographs is sometimes a difficult task and the same applies to intensity measurements which are required in the disappearing-phase method. There are also situations in which the X-ray methods yield erroneous results unless supported by other data on the alloy system being explored (40). The simplicity of the optical or microscopic method is a decided advantage, and consequently it was used in this investigation.

Examination of As-Melted Structures

Examination of the first series of alloys in the as-melted condition was undertaken to obtain all possible information on the nature of the equilibrium diagram and to determine what additional alloy compositions should be studied. The uniformity of the microstructure is also a rough indication of homogeneity, another factor about which information is always desirable.

The first alloys studied are listed below for convenience:

Heat No.	Intended Composition (Wt. percent Cu)	Composition by Analysis (Wt. percent Cu) ^a
1	0	0
2	2.0	5.96
5	3.6	3.94
8	5.1	5.86

^aThe method used for analyzing the alloys is described in the appendix.

These alloys were melted in a hemispherical copper crucible which permitted the charge to split into separate puddles during the melting operation. Alloys 3, 4, 6 and 7 were immediately rejected for this reason. Modifying the crucible cross section as shown in Figure 1 eliminated this difficulty.

A number of etching reagents were successfully employed in these preliminary examinations. For convenience, the compositions of three of these were designated A, B and C etch respectively:

(A-etch) HF(48percent), HNO_3 (conc.), glycerol (1:1:2).

(B-etch) HF(48percent), glycerol (1:1).

(C-etch) HF(48percent), HNO_3 (conc.), H_2O (3:7:90).

All photographic work was done under bright field illumination.

Commercially pure titanium exhibits one of two varieties of an acicular structure when cooled rapidly from above the allotropic transformation temperature (63). Both of these transformation products were observed. Sample 1 (unalloyed commercially pure titanium) was composed entirely of parallel acicular alpha titanium (Figures 2 and 3) while the non parallel acicular form was displayed by alloy 5 (Figure 4). No excessive amount of inclusions above and beyond that normally exhibited by commercial titanium was apparent in any of the ingots (Figure 5).

Despite its obvious inhomogeneity, the as-cast microstructure of alloy 2 reveals an interesting situation (Figures 6 and 7). There are at least two different white-etching constituents present, one of which was polished in relief indicating that it is of a higher hardness than the matrix. Intermetallic compounds frequently exhibit this behavior and at least one intermetallic compound is known to be present in the titanium-



FIGURES 2 and 3

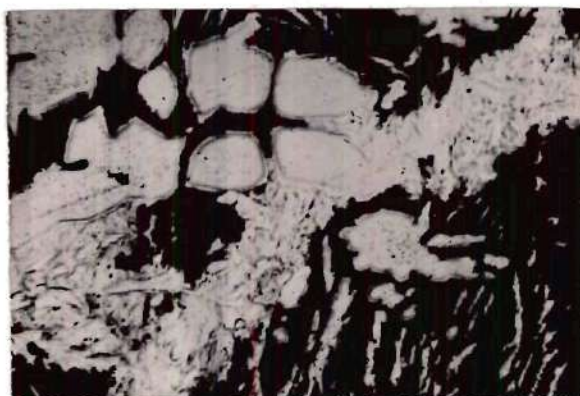
Commercially pure titanium, as-melted, B-etch. Figure 2 (top), X 100; Figure 3 (bottom), X 500. This structure is similar to the parallel acicular alpha titanium obtained by rapid cooling through the allotropic transformation temperature (63).



FIGURES 4 and 5

Figure 4(top), Ti-Cu alloy (3.94 percent Cu), B-etch, X 250.
Non-parallel acicular alpha titanium obtained by rapid cooling through
the transformation range.

Figure 5(bottom), inclusions in alloy 8 (5.86 percent Cu), as-
melted, C-etch, X 500,



FIGURES 6 and 7

Alloy 2 (5.96 percent Cu), as-melted, C-etch. Figure 6 (top), X 250; Figure 7 (bottom), X 1000. At least two white-etching constituents are visible, one of which appears to be polished in relief.

copper system (72).

With the exception of alloy 2 (Figures 6 and 7), the samples appeared to be reasonably homogenous. No conclusive information regarding the phases present at equilibrium could be ascertained from this examination of the as-cast structures.

Equilibrium Microstructures

Microscopic examination of a specimen annealed 16 hours at 1600°F showed that transformation had occurred. Compare Figures 2, 3 and 8. At this temperature, a thin, dense and firmly adherent bronze-colored film was easily removed by grinding and no inward diffusion was apparent.

The other alloys of this series were annealed under the above conditions and furnace cooled. After the metallographic polishing operation described earlier, the annealed specimens were studied under the microscope.

A microphotograph of alloy 5 shows a "basket weave" pattern of alpha solid solution outlined by a darker etching constituent (Figure 9). The same dark material was present to a greater extent in alloy 8 (5.86 percent Cu). When examined under high (2000X) power, these dark areas plainly showed the lamellar structure characteristic of a eutectoid mixture (Figure 10). The increased amount of the eutectoid present in alloy 8 over that in alloy 5 shows that both are in the hypo-eutectoid range.

In an effort to locate the solvus line and the eutectoid composition, additional alloys of the following compositions were melted and annealed immediately afterward:



FIGURE 8

Polygonal alpha titanium grains, sample 1 (unalloyed), after annealing in air at 1600°F for 16 hours and furnace cooling. Comparison of this structure with that of the as-melted condition (Figures 2 and 3) shows that the acicular pattern has been completely obliterated. B-etch, X 100.



FIGURE 9

Alloy 5 (3.94 percent Cu) after annealing 16 hours at 1600°F followed by furnace cooling. C-etch, X 100. The varying degrees to which the lighter-etching material is darkened by the etching reagent identify it as the solid solution of copper in alpha titanium (63). Beta titanium is not affected by this etching reagent and the dark network must therefore be a eutectoid mixture.

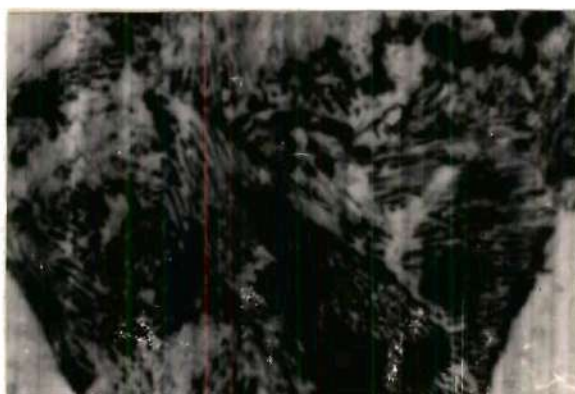


FIGURE 10

Same as Figure 9, X 2000. The eutectoid lamellae in the dark-etching network of Figure 9 are plainly visible. The solid solution of copper in beta titanium has decomposed at some higher temperature to yield alpha solid solution and another phase.



FIGURE 11

Ti-Cu alloy, 6.27 percent Cu, C-etch, X 100. Alpha solid solution (white) and eutectoid (dark). The increased amount of eutectoid over that in alloy 5 and the presence of a smaller proportion of alpha shows that the eutectoid composition is being approached.



FIGURE 12

Ti-Cu alloy, 9.83 percent Cu, C-etch, X 500. This alloy lies almost exactly upon the eutectoid composition. A very small amount of proeutectoid alpha was visible at higher magnifications.

Heat No.	Intended Composition Wt. percent Cu	Composition by analysis Wt. percent Cu
10	1.5	1.81
11	9.8	9.84
12	7.1	6.28
13 ^B	0.33	--
14	0.25	0.35
15 ^C	0.76	--
16	0.68	0.97

After annealing, alloy 10 (1.81 percent Cu) still showed traces of the eutectoid structure, while numbers 15 and 16 each showed a two-phase structure with no eutectoid present (Figure 14).

Utilizing the data of Craighead, Simmons and Eastwood (15) as a starting point, quenching tests were carried out as described earlier. Results are shown graphically in Figure 13, the proposed thermal equilibrium diagram for this alloy system.

Efforts to make a close estimate of the solvus line were unsuccessful. Even after solution heat treatment at 1800°F for 88 hours and slowly cooling to the range 1450 - 1550°F followed by quenching, the two-phase structure of alloys 15 and 16 persisted. The duplex appearance of these alloys was shown to be due to a second phase by taking Bergsman microhardness readings on the two areas in question (Figure 14). For the large

^BAlloy 13 was rejected when the copper alloying addition failed to fuse properly.

^CAlloy 15 was not analyzed as it displayed virtually the same microstructure as alloy 16. See Figure 14.

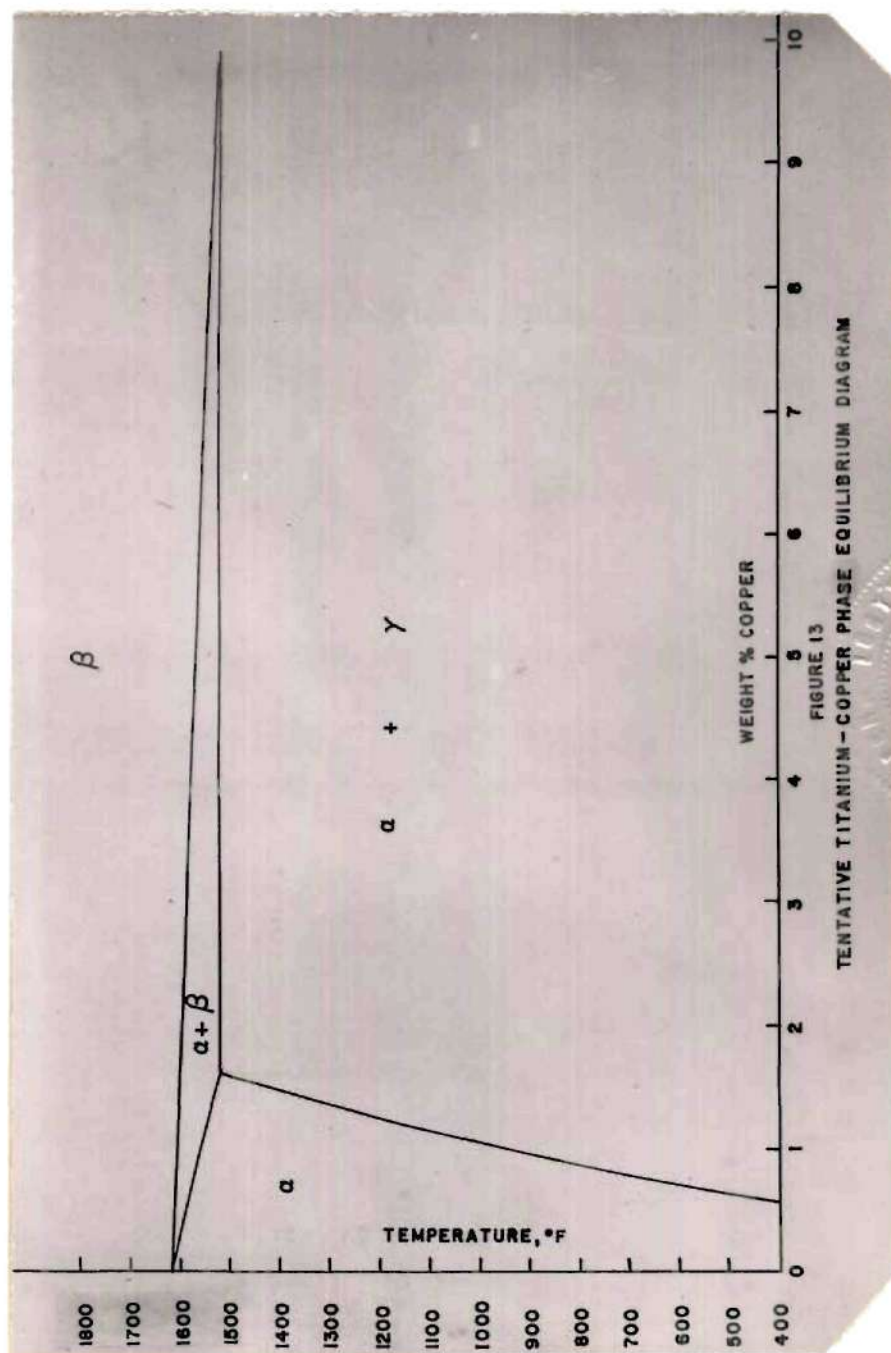


FIGURE 13



FIGURE 14

Alpha (dark) and gamma (light) in a Ti-Cu alloy analyzing 0.97 percent Cu. after annealing at 1600°F for 16 hours and furnace cooling. B-etch, X 250. The striated appearance of the alpha grains shown above is due to the action of the etching reagent. The absence of the eutectoid structure in this alloy indicates that the gamma was precipitated from the alpha on cooling.

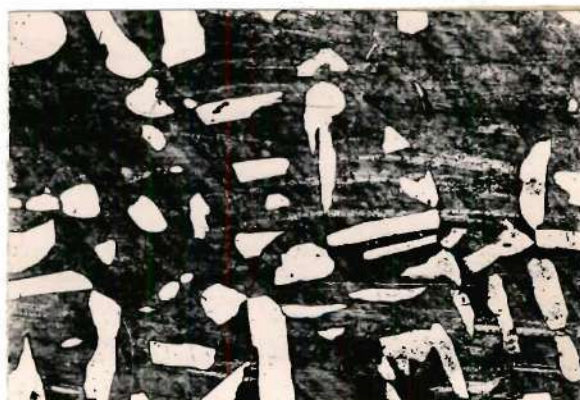


FIGURE 15

Alloy 5 (3.94 percent Cu) B-etch, X 100. Quenched from 1600°F in the beta field. A portion of the beta (white) has been retained while the balance decomposed into acicular alpha (dark). The retained beta could be distinguished from alpha only by the application of the above etching reagent which outlined the retained beta.

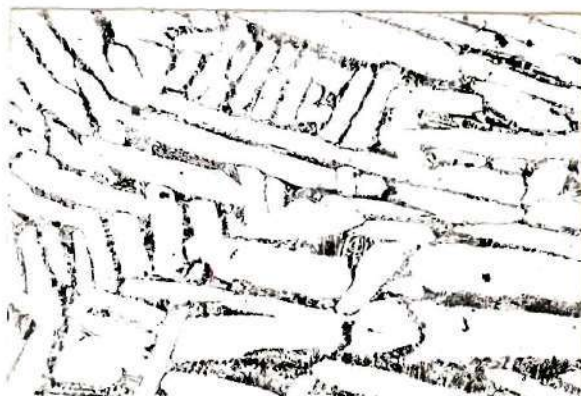


FIGURE 16

Alloy 5 (3.94 percent Cu), B-etch, X 100. Quenched from 1500°F, just below the eutectoid temperature. Prolonged annealing in this temperature range results only in a coursening of the eutectoid and an increase in grain size. Compare with Figure 9.

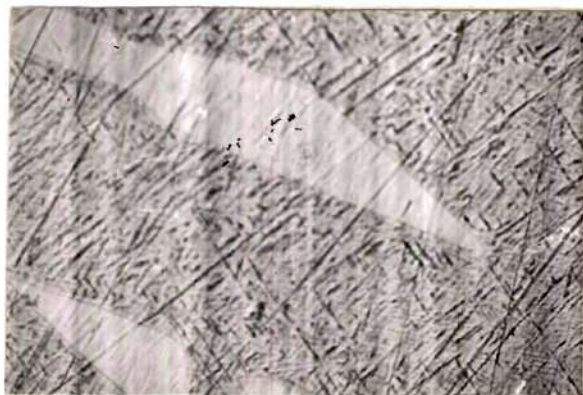


FIGURE 17

Ti-Cu alloy, 3.94 percent Cu, B-etch, X 250. Quenched from 1700°F in the beta field. The acicular nature of the decomposed beta is clearly evident in this view. The alignment of the retained beta suggests that decomposition to the acicular alpha in a quench occurs not only at the beta grain boundaries but along certain crystallographic planes within the beta grains as well.

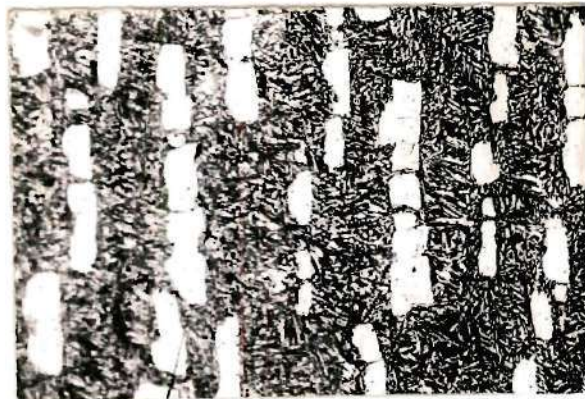


FIGURE 18

Eutectoid alloy (9.84 percent Cu) quenched from 1800°F in the beta field. B-etch, X 100. The dark constituent surrounding the retained beta (white) appears to be a modification of the eutectoid structure rather than the acicular alpha obtained by subjecting hypoeutectoid alloys to a similar treatment. See Figures 15 and 17.

dark (alpha) areas a Vickers hardness of 307 (Rockwell A 66) was obtained. Impressions on the light network showed that it possessed a much higher hardness, Vickers 430 (Rockwell A 72). This high variation in hardness indicates that the precipitated gamma phase may be a compound of copper and titanium, possible Cu_3Ti (72).

The hardness value obtained for the alpha phase of the above alloys is comparable with a value of Vickers 326 reported for the alpha phase in a titanium-base alloy containing 0.78 percent carbon. Titanium carbide in the same alloy failed to respond to solution heat treatment as did the gamma phase of the Ti-Cu system throughout this investigation (54).

Discussion of Results

The portion of the titanium-copper thermal equilibrium diagram which was determined by these experiments exhibits no striking peculiarities. It is seen to be of the same form as the lower portion of the iron-rich side of the familiar iron-carbon system. The possibility that the beta phase might decompose eutectoidally was predicted in Chapter III.

A study of the low-copper alloys in which solid-phase precipitation had occurred indicated that the solubility of copper in alpha titanium increased from a value at room temperature lying between 0.35 - 0.97 percent Cu to a maximum at the eutectoid temperature (1520°F) of slightly less than 1.81 percent Cu. An alloy of the latter composition displayed only minute traces of the eutectoid. This variation of solid solubility indicates that hypoeutectoid alloys of this system have potential age-hardening characteristics. Craighead et.al. found copper alloys of titanium up to 4.85 percent copper to respond noticeably to this treatment and pointed out that alloys of higher copper contents might be hardenable to

a greater extent (15).

The metallography of this system is similar to that of the titanium-nickel system in one respect (52). Additions of copper apparently decrease the tendency of the beta high-temperature solid solution to decompose during a quench. This is shown in Figure 15, a view of alloy 5 (3.94 percent Cu) quenched from the beta field. In a situation of this sort, it is necessary to utilize the contrast afforded by B-etch. This reagent will darken any alpha solid solution present and only outline the retained beta as shown in Figure 15. Quenching the same alloy from just below the eutectoid temperature (1500°F) resulted only in an increase in grain size and a coarsening of the eutectoid. Compare Figures 9 and 16.

The type of equilibrium microstructure exemplified by the alloys shown in Figures 9 and 11 is called a Widmanstätten structure or pattern. It was first observed in meteoric iron in 1808 by the French scientist whose name it bears (56). The peculiar "basket weave" appearance of this structure comes into being as the transformation range is traversed in cooling. When an alloy cooling from the beta region reaches the upper temperature limit of the transformation range, the alpha or other proeutectoid constituent begins to form at the grain boundaries of the beta phase and also along certain crystallographic planes within individual beta grains. These plates of the proeutectoid constituent have a lower capacity for copper than the surrounding beta so that as they grow in size and number the residual beta approaches and finally reaches the eutectoid composition. This tendency for the proeutectoid phase to form along certain preferential planes in the beta lattice accounts for their alignment. Precipitated phases which comes into being in this manner

bear a definite crystallographic relationship to the parent solid solution (60). Figures 15 and 17 indicate that the decomposition of beta in a quench proceeds according to a similar mechanism.

An additional point of interest is the appearance of annealed alpha titanium under polarized light. When viewed under these conditions, lightly etched (reagent A) grains of alpha titanium such as are shown in Figure 8 show striking differences in color. A cyclic change in color of individual grains may be observed if the metallograph stage is rotated through forty five degrees. This same effect has been observed in aluminum and certain of its alloys. In the case of aluminum it is known to be due to the presence of an anodic oxide film which is optically anisotropic to polarized light (37).

Copper additions appear to affect the scaling characteristics of titanium markedly. In the low (0 - 3.94 percent) copper alloys a hard bronze-colored outer scale formed upon prolonged annealing in air. Beneath this layer a very thin grayish scale was found which had to be removed by grinding. Alloys of higher copper contents under identical conditions of exposure appeared to exhibit a lesser tendency to scale. No visible inward migration of the oxide or nitride was apparent in any of the alloys studied.

Conclusions and Recommendations

It is believed that the following conclusions based upon this investigation are warranted:

- (1) The high-temperature (beta) solid solution of copper in titanium decomposes eutectoidally upon slowly cooling from the beta region. The eutectoid temperature and composition are approximately 1520°F and

9.84 percent copper respectively. Copper additions depress the allotropic transformation temperature range as shown in Figure 13.

(2) The solubility of copper in alpha titanium increases with increasing temperature from a value lying between 0.35 - 0.97 percent copper to a maximum of slightly less than 1.81 percent copper at the eutectoid temperature, 1520°F.

It is recommended that future work in this field be directed along the following channels:

(1) The construction of a larger melting furnace which would make possible the fusion of larger specimens. From these ingots, suitable test specimens could be fabricated and an evaluation of the mechanical properties of alloys of this system could be undertaken.

(2) The increase in solid solubility of copper in titanium with an increase in temperature indicates that the hypoeutectoid alloys are potentially age-hardenable, a fact confirmed by Craighead et.al. (15). In addition to exploiting this possibility further, the quench-hardening characteristics of alloys lying near the eutectoid composition should be studied.

(3) The effect of other alloying elements should be investigated. Of particular interest would be ternary additions of elements which are known to form intermetallic compounds with either or both titanium and copper. The formation of such compounds would in all probability enhance the age-hardening characteristics of this system. Other desirable changes in mechanical properties might be achieved by the addition of other components.

(4) The apparent change in character of the scale formed on an-

nealing with increasing copper content merits further study. It is possible that copper inhibits the oxidation of titanium at elevated temperatures. In this connection, the corrosion properties of these alloys should also be studied.

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APPENDIX

TABLE I
PHYSICAL PROPERTIES OF IODIDE TITANIUM (31)

Quantity	Unit	Temperature, °F	Value
Atomic Number			22
Atomic Weight			47.90
Density	gm/cm ³	68	4.507
Crystal Structure	Angstroms	Room Above 1615	H.C.P., a= 2.946, c= 4.686 B.C.C., a= 3.32
Melting Point	°F		3150
Boiling Point	°F		above 5400
Resistivity	ohm-cm.	68	4x X 10 ⁻⁶
mean	cal/gm.	32 - 426	0.1291
specific		32 - 510	0.1316
heat		32 - 608	0.1334
		32 - 932	0.1386

TABLE II
MECHANICAL PROPERTIES OF IODIDE AND
COMMERCIAL TITANIUM (31)

<u>Annealed Conditions</u>	<u>Iodide</u>	<u>Mg. Reduced</u>
Ultimate Strength, psi	38-48,000	80,000
Yield, 0.2 percent Offset, psi	20-24,000	72,000
Prop. Limit, psi	10,000	38,000
Elongation, percent	40 (1")	25 (2")
Red. in Area, percent	75	55
Mod. of Elasticity, psi	14-1515 X 10 ⁶	16-16.5 X 10 ⁶
<u>Cold Worked, 50 percent Reduction</u>		
Ultimate Strength, psi	97,000	125,000
Yield, 0.2 percent Offset, psi	87,000	110,000
Elongation, percent	11 (1")	12 (2")
Red. in Area, percent	75	30
Cold rolling before edge cracking, percent	95+	50-60

ANALYTICAL METHODS

In order to determine alloy compositions to the desired degree of accuracy, a method of chemically analyzing the alloys studied in this investigation was desirable. Much has been written on the analytical chemistry of titanium^a but very little deals specifically with the determination of copper in titaniferous substances. However virtually any textbook on quantitative analysis discusses at least three means of separating titanium from copper and other metals. By boiling a mildly acid solution of titanium and copper salts, titanium may be precipitated as the hydrated oxide. Copper may be precipitated from a slightly acid solution in the presence of a soluble tartrate by the use of a soluble sulfide or H_2S . The copper can also be replaced in solution by a more active metal without interference by titanium (44).

Time limitations did not permit more than a superficial study of the above methods as applied to titanium-copper alloys. The hydrolysis of titanium in acid solution was attempted but abandoned when tests on mechanical mixtures of titanium and copper indicated that copper was being coprecipitated. The titanium dioxide precipitate was colloidal in nature and difficult to remove by filtration. The separation recommended by Low (53) involving the replacement of copper by aluminum was attempted but proved unsuccessful. It appeared that the aluminum salts formed would hydrolyze under the conditions necessary to prevent the hydrolysis of titanium. Trial runs using the sulfide precipitation for removing the copper followed by iodometric titration of the copper indicated that this separation is effective.

^aAn extensive bibliography on the analytical chemistry of titanium is given in reference (4).

The analytical procedure as finally evolved by testing mechanical mixtures of copper and titanium consisted first of sampling the alloy to be analyzed. Several small holes were drilled at random locations over the ingot after homogenization and the resulting chips collected. These chips were rinsed in alcohol and air dried several hours to remove any oil or grease picked up during drilling. A weighed portion of the chips was then slowly digested in dilute hydrofluoric acid. It was found desirable to begin the digestion in a very slightly acid solution (5 percent by volume) and add hydrofluoric acid (technical grade, 48 percent) in two-drop increments until the bubbling action ceased.

When digestion was complete the solution was diluted to 50 ml. and two grams of tartaric acid added. When the tartaric acid was dissolved completely, concentrated sodium sulfide solution was added until the precipitation of copper sulfide was complete.

The precipitate, after filtering and washing with dilute sodium sulfide solution, was ignited in a small crucible over a low flame until the filter paper was ashed off completely. The residue remaining in the crucible was leached with boiling dilute (1:1) nitric acid and filtered.

The filtrate was boiled vigorously to remove any lower oxides of nitrogen. As an additional precaution, 5 ml. of bromine water was added to insure complete removal of the oxides of nitrogen. After further boiling to remove the excess bromine, the solution was made alkaline with a slight excess of ammonium hydroxide and again boiled to the disappearance of the deep blue color. Twenty ml. of 6 N acetic acid were added and the solution transferred to a volumetric flask where it was diluted to the desired volume. Aliquot portions were withdrawn by pipet for iodometric

titration.

The iodometric titration of copper is described in detail in virtually any textbook on quantitative chemical analysis, and for that reason will not be discussed here.

Every effort was made to utilize reagents of the highest purity obtainable. The starch used in the indicator solution was a water-soluble variety marketed especially for use as an indicator in iodometric titrations. The sodium thiosulfate was standardized prior to use against metallic copper at various points during the analytical runs.

The results obtained have been tabulated earlier and are erratic in nature when compared with the composition of the initial charge. This is attributable to the tendency of titanium to splatter during melting. In some cases, copper was lost by the same process. Efforts were made to minimize this splattering by elevating the electrode after striking the arc and allowing the absorbed gases to escape prior to melting. This was difficult to accomplish but some success was achieved by slowly fusing the charge. Alloys 10 and 11, for example, were known prior to their preparation to lie very near the point of maximum solid solubility and the eutectoid composition respectively. Consequently the above precautions were observed while melting them and the analytical results are fairly consistent with the charge compositions.